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(54) Title: **COMPOSITIONS FOR NON-POLLUTING FUELS, PREPARATION PROCESSES AND USE THEREOF**

(57) Abstract: The present invention relates to a composition for diesel fuels/combustibles, which comprises a hydrocarbon fluid component, a component made of plant and/or animal material or a derivative thereof, which is suitable for use as a fuel and/or combustible, and optionally water, surfactants and stabilizers, in which the said hydrocarbon fluid consists of a mixture of paraffinic, isoparaffinic and cycloparaffinic hydrocarbons containing more than six carbon atoms in the molecule, that is substantially free of aromatic compounds and that is obtained by hydrogenation and distillation of petroleum fractions.

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COMPOSITIONS FOR NON-POLLUTING FUELS, PREPARATION
PROCESSES AND USE THEREOF.

5 DESCRIPTION

The present invention relates to compositions for non-polluting fuels for diesel engines and combustion or heating plants, to processes for preparing them and to
10 their use.

Traditional liquid combustibles/fuels for internal combustion engines consist of mixtures of hydrocarbons mainly derived from mineral oils. In view of the
15 limited reserve of mineral oils and the expanding costs of crude oil, there is an increasing demand for fuels that can replace petroleum-based hydrocarbons or that allow the existing resources to be used more efficiently.

20 The high level of environmental pollution caused by the polluting components contained in the exhaust gases of internal combustion engines, in particular hydrocarbons, carbon monoxide, nitrogen oxides (NO_x) and sulphur oxides (SO_x) and carbon particulates, has
25 led to the search for alternative fuels that are less polluting and that are capable of replacing or reducing the proportion of petroleum-based fuels conventionally used.

30 Diesel engine fuels defined as being non-polluting are known, such as gas oil in unmodified form with a very low sulphur content and also gas oil combined with a percentage of plant or animal oils and derivatives
35 thereof, for example the methyl ester of plant oil and fatty acids (commonly known as biodiesel).

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White diesel fuels are also known, which are obtained as an emulsion in water of gas oil with a very low sulphur content, in which the water is accompanied by one or more additives.

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However, the use of such fuels still produces a high level of emissions, from the combustion chamber of the internal combustion engine, of CO, micro- and macro-particulates, SO₂, NO and NO₂, carbon-based residues, heavy metals and polycyclic aromatics.

10

Furthermore, these fuels are poorly biodegradable.

The task of the present invention is, precisely, to eliminate the drawbacks of the known fuels and to provide a fuel/combustible composition for use in any type of diesel engine, in any type of vehicle and in any combustion plant, that is biodegradable and less polluting than traditional diesel fuel.

20

In particular, one aim of the present invention is to provide compositions for diesel fuels/combustibles that produce exhaust gases with a low (or even undetectable) level of sulphur-containing compounds.

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Another aim of the present invention is to provide compositions for diesel fuels/combustibles characterized by a low emission of particulates in the exhaust gases.

30

A further aim of the present invention is to provide compositions for diesel fuels/combustibles that have a low content or are even free of aromatic compounds, and that do not require cetane-number improvers.

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Another characteristic of the present invention is that of providing a diesel fuel/combustible that can be

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formulated either in "standard" version or in winter or "arctic" version, enabling any diesel engine to be fed without intervention on or modification of the engine or of the regulation of the pump system and/or of the filter system.

Another aim of the present invention is to provide a composition for diesel fuels/combustibles that can withstand temperature variations in line with the natural course of the ambient temperature without showing any separation of water or additives, as normally takes place with various fuels that are already known and that emulsified or mixed by conventional means and techniques.

This task and these aims, and other aims that will become clear from the description of the invention which follows, are achieved by means of a fuel/combustible composition according to the attached claims.

The composition of the present invention is a composition for diesel fuels/combustibles, which comprises a hydrocarbon fluid component, a component made of plant and/or animal material and/or a derivative thereof, which is suitable for use as a fuel, and optionally water, surfactants and stabilizers.

In one embodiment, the composition of the present invention contains water and is in the form of an emulsion.

The hydrocarbon fluids used in the compositions of the present invention consist of mixtures of paraffinic, isoparaffinic and/or cycloparaffinic hydrocarbons, and are substantially free of aromatic compounds. In

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particular, the hydrocarbon fluid of the present invention comprises a mixture of hydrocarbons. Preferably, the hydrocarbons contain more than six carbon atoms in the molecule. The content of aromatics in the hydrocarbon fluid used in the present invention is less than 0.2% by weight, and the sulphur content is less than 10 mg/kg.

The hydrocarbon fluid may be derived from a petroleum middle distillate subjected to dearomatization, with a narrower distillation range than automotive gas oil, and which, when used in unmodified form, does not exceed the standards in force for automotive gas oils.

The hydrocarbon fluid used in the composition of the present invention may be obtained by hydrogenation and distillation of petroleum fractions.

A hydrocarbon fluid that is particularly advantageous for use in the fuel/combustible compositions of the present invention is chosen from the group consisting of mixtures of dearomatized hydrocarbons, obtained from the refining of petroleum, having the following characteristics:

- flammability point: from 30°C to 150°C
- boiling range: from 140°C to 270°C
- range of the distillation cut: from 5 to 50°C.

An example of a hydrocarbon fluid that is suitable for use in the compositions of the present invention is known as EXCS1, and its typical properties are given in Table 1.

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TABLE 1

Property	Measuring unit	Minimum values	Maximum values	Typical values	Test method (the last method, unless otherwise indicated)
Distillation range Final boiling point	°C	200	250.0	237	ASTM D 86
Flammability point	°C	70.0		75	ASTM D93
Content of aromatics (UV) *	wt%		0.2000	0.08	EC-A-A07
Saybolt colour	-	+30		+30	ASTM D 156
Sulphur content	mg/kg		5.0	<1	ASTM D 4045
Viscosity at 40°C	mm ² /s	1.50	1.70	1.63	ASTM D 455 modified
Density at 15°C	kg/dm ³			0.806	ASTM D 4052
Refractive index at 20°C				1.443	ASTM D 1218
Viscosity at 25°C	mm ²			2.09	ASTM D 445 modified

In particular, the hydrocarbon fluid used must be capable of forming a micronized emulsion with water, preferably demineralized water, and also with the plant and/or animal material.

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The plant and/or animal material that is suitable for use in the composition of the present invention is preferably chosen from the group consisting of plant oils, for instance sunflower oil, soybean oil, palm oil, fatty acids of plant or animal nature and/or derivatives thereof, for instance the methyl esters, commonly known as biodiesels.

A preferred example is the methyl ester of plant oil or fatty acids that satisfies the specifications UNI-10635, CUNA-E03.50.617.0, or standards in force in any other state, such as France or Germany or the CEC standards at Community level.

Typical properties of a methyl ester of plant oil that is suitable for use in the present invention are given in Table 2, in line with the specifications UNI 10635/CUNA E 03.50.617.0.

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TABLE 2

CHARACTERISTIC	MEASURING UNIT	VALUE		TEST METHOD
		Min.	Max.	
Appearance at 20°C		Clear		Visual examination
Acidity	mgKOH/g	-	0.5	UNI 22049
Water	ppm	-	700	ISO 6296
Ash	% m/m	-	0.01	ISO 6245
Distillation:				ASTM D 86
- initial point	°C	300	-	(modified)
- distilled to 95% by volume	°C	-	360	
Density at 15°C	Kg/m ³	860	900	ISO 3675
Phosphorus	ppm	-	10	UNI 22050
Bound glycerol				UNI 22053
Monoglycerides	% m/m	-	0.8	
Diglycerides	% m/m	-	0.2	
Triglycerides	% m/m	-	0.1	
Free glycerol	% m/m	-	0.05	UNI 22054
Methanol	% m/m	-	0.02	UNI 22048
Methyl ester	% m/m	98.0	-	UNI 22053
Saponification No.	mgKOH/g	170	-	UNI 22051
Flammability point	°C	100	-	EN 22719
Yield value	°C	-	0	ISO 3016
Conradson carbon-based residue (on 10% distillation residue)	% m/m	-	0.5	ISO 6615
Viscosity at 40°C	mm ² /s	3.5	5	ISO 3104
Sulphur	% m/m	-	0.01	EN 24260

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The water used in the compositions of the present invention is preferably deionized or demineralized water.

- 5 The compositions of the present invention also contain surfactants and emulsion stabilizers, of various types.

The compositions of the present invention contain no silicon-based compounds.

10

Preferably, the surfactants are nonionic surfactants, for example unmodified or ethoxylated or propoxylated fatty acids and/or ethoxylated or propoxylated plant oils and/or an alcohol containing from 8 to 22 carbon atoms, ethoxylated or propoxylated with from 2 to 15 mol of ethylene oxide or propylene oxide, or any other nonionic surfactant.

It is possible to use different ethoxylation or propoxylation or to use other synthetic or natural chemical compounds, ethoxylated or propoxylated with varying degrees of ethylene oxide or propylene oxide, for instance ethoxylated or propoxylated nonylphenol, ethoxylated or propoxylated methyl esters, polyglycols, etc., or other nonionic emulsifiers.

The stabilizers that may preferably be used are polyols in pure or mixed form or partially esterified with fatty acids, that are themselves in pure or mixed form. Examples include sorbitan or sorbitol mono- or sesqui- or dioleate, which may or may not be ethoxylated and/or propoxylated.

The compositions of the present invention may contain further additives.

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In one preferred embodiment, the composition for diesel fuels/combustibles of the present invention contains:

1. Hydrocarbon fluid: 100 parts by volume
2. Plant oil and/or plant oil derivative and/or fatty acids and/or fatty acid derivatives, the fatty acids being of any origin: 5-90, preferably 10-80, more preferably 6-50 parts by volume per 100 parts of hydrocarbon fluid
3. Demineralized water: 0-30, preferably 2-25, more preferably 5-15 parts by volume per 100 parts of hydrocarbon fluid
4. Surfactant and stabilizer preferably of plant type (possibly with a coadjuvant): 0-4 parts by volume per 100 parts of hydrocarbon fluid.

In the present invention, the plant and/or animal material is a true component of the fuel composition, as opposed to an additive.

In particular, a composition having the formulation below was tested, which is not preferential but typical for an ambient temperature that is not less than -5°C.

1. Hydrocarbon fluid: 71.5%
2. Methyl ester of plant oils: 17.8%
3. Demineralized water: 8.9%
4. Stabilizer of organic type: 1.3%
5. Surfactant (C_{16} - C_{18} alcohol with 120 mol of ethylene oxide): 0.5%.

Specifically, the fluid has the characteristics given in Table 1, the methyl ester of plant oil is a methyl ester of rapeseed oil, the stabilizer is sorbitan mono-oleate and the surfactant is an ethoxylated C_{16} - C_{18} alcohol.

The fuel of the present invention is biodegradable and has the following physicochemical properties:

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CFPP	< -12°C
Pour point	< -20°C
Cetane No.	> 48
Mean calorific power	> 35 Mjoules/kg
5 Distillation curve	IBP > 100°C
	FBP < 400°C
Flash point	> 60°C
Density at 15°C	< 1 000 kg/m ³ .

- 10 The compositions of the present invention have intrinsic energy characteristics and therefore do not require an addition of conventional gas oils, although these may be added. If present, the conventional gas oils derived directly from petroleum may be present in
15 an undetectable percentage.

The compositions of the present invention may be prepared as a winter (ARCTIC) formulation.

- 20 In this case, the composition also comprises from 0.1% to 10% by volume of monoethylene glycol relative to 100 parts by volume of the total composition. The formulation indicated may undergo variations in relation to the physicochemical behaviour of the
25 components at various temperatures, while nevertheless maintaining the combustibility and oxidation characteristics.

- The winter (ARCTIC) formulation of the compositions of
30 the present invention are suitable for use at temperatures between -35°C and -5°C.

- The diesel fuel/combustible compositions of the present invention may be prepared by any traditional mixing
35 process, and in particular that used for the preparation of microemulsions.

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One method that is preferred for producing the compositions for diesel fuels/combustibles of the present invention in emulsion form is a method by means of which high productivity and stability may be
5 instantaneously achieved. This can usually be obtained using suitable devices, known as continuous differential homogenizers (abbreviated as CDH), which are fed by suitable electropumps, equipped with accessories such as, for example, a static system with
10 dynamic flows operating by a turbine effect through in-line cavitation chambers, of the type with inverted flow, so as to obtain homogeneous microcells of not more than 0.20 micron.

Before entering the specific "CDH" device, the fluids
15 are pre-metered by automatic systems and are then filtered.

The exhaust gases of a fuel/combustible according to the present invention for diesel engines, known as
20 "White-Fuel®", were subjected to instrumental analysis using a homologated analyser according to standard UNI-10389, performed, for example, on a diesel engine even of small engine size (1600 cc turbodiesel, thus an engine that is rather penalized relative to a lorry or
25 coach engine of greater power and size), and showed in relation to the usual analyses the following instantaneous parameters under the climatic and temperature conditions indicated below:

- Altitude	300 m above sea level
30 - Temperature	19-20°C
- Exhaust gas temperature	139-154°C
- O ₂	16.2-17.4% approximately
- CO ₂	3.5-2.3% approximately
- CO	214 ppm
35 - NO-NO ₂ (NO _x)	79 ppm
- SO ₂	0 ppm

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- Opacity (Article 615) 20-22.1 (this parameter is markedly better for a coach engine and/or the like)
- 5 - Particulates < 10 mg/m³
- Opacity as Bacharach No. < 1

In addition, experimental tests on a diesel fuel/combustible composition according to the present invention, the product "White Fuel[®]", demonstrate that the compositions of the present invention amply satisfy the requirements of the standard CUNA NC637-01 of March 2000 which characterizes water-in-gas oil emulsions for automotive use.

15

In addition, tests carried out on the winter formulation of the diesel-fuel compositions of the present invention, performed by maintaining the product "White-Fuel[®]" in frozen form at a temperature below -35°C for 24 hours, followed by returning it to an ambient temperature of +18°C, showed that the winter formulation of the compositions, after having undergone a course of natural changes in ambient temperature, show no separation of water or additives, as takes place, however, with various known fuels which are emulsified or mixed by conventional means and methods.

25

The compositions for the diesel fuels/combustibles of the present invention may be advantageously used as fuels/combustibles for any diesel engine, used in any type of vehicle or craft, or alternatively for combustion and heating.

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When compared with conventional diesel fuel, the compositions of the present invention are advantageous in that they have low (or even undetectable) levels of sulphur-containing compounds in the exhaust gases, low

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emissions of particulates in the exhaust gases, they do not require cetane improvers and they are readily biodegradable. The use of the compositions of the present invention in diesel engines does not require
5 particular modifications or regulations of the engine, and in particular the injection pumps, gaskets and filtering systems do not need to be changed.

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CLAIMS

1. Composition for diesel fuels/combustibles, which comprises a hydrocarbon fluid component, a component made of plant and/or animal material or a derivative thereof, which is suitable for use as a fuel and/or combustible, and optionally water, surfactants and stabilizers, in which the said hydrocarbon fluid consists of a mixture of paraffinic, isoparaffinic and cycloparaffinic hydrocarbons, that is substantially free of aromatic compounds and that is obtained by hydrogenation and distillation of petroleum fractions.
2. Composition according to Claim 1, in which the said animal or plant material consists of a plant and/or animal oil and/or fatty acid, and/or a derivative thereof.
3. Composition according to Claim 1 or 2, which comprises
- hydrocarbon fluid: 100 parts by volume
 - plant and/or animal oil and/or a derivative thereof: from 1 to 50 parts by volume
 - water: from 0 to 30 parts by volume
 - surfactants and stabilizers: not more than 4 parts by volume.
4. Composition according to any one of the preceding claims, in which the said hydrocarbon fluid is chosen from the group consisting of dearomatized hydrocarbons obtained by refining petroleum, with a flammability point of 30°C to 150°C, a boiling range of between 140°C and 230°C, and a range of the distillation cut of from 5 to 50°C.

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5. Composition according to Claim 2, in which the said plant oil is chosen from the group consisting of rapeseed oil, sunflower oil, soybean oil, palm oil and the methyl ester of rapeseed oil, and/or the methyl esters thereof in pure and/or mixed form.
6. Composition according to Claim 2, in which the said plant material is a methyl ester of a plant oil.
7. Composition according to Claim 1, in which the said surfactants are nonionic surfactants, preferably ethoxylated alcohols.
8. Composition according to Claim 1, in which the said stabilizer is chosen from the group consisting of partially esterified polyols that are in unmodified form and/or ethoxylated and/or propoxylated, and/or mixtures thereof.
9. Composition according to Claim 1, comprising
- hydrocarbon fluid: 71.5%
 - methyl ester of plant oils: 17.8%
 - demineralized water: 8.9%
 - stabilizer: 1.3%
 - surfactant: C₁₆-C₁₈ alcohol with 120 mol of ethylene oxide: 0.5%.
10. Composition according to Claim 1, which also comprises monoethylene glycol, preferably at from 0.1% to 10% by volume relative to the water.
11. Composition according to Claim 1, also comprising conventional gas oil.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/02 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 520 708 A (JOHNSON LAWRENCE A ET AL) 28 May 1996 (1996-05-28) claims 1-3 column 2, line 65 -column 3, line 2 column 3, line 47 - line 58 example 6	1-3,5,6, 11
A	WO 99 63026 A (CATERPILLAR INC) 9 December 1999 (1999-12-09) claims 1,6-9	1,3,7
A	US 5 506 272 A (YAKOBSON DENNIS L ET AL) 9 April 1996 (1996-04-09) claim 1	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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